EXERCISE 2

A Computation of the SiO Bond Lengths and Angles for a Silica polymorph: A Study of Bond Length and Angle Variations and SiO Bonding Models

"Of all the properties of silica that depend in some way on the nature of its binding forces, only a handful can be uniquely identified with an individual bond. Of these, bond length is special in the sense that it provides a reliable measure of the strength of a bond: the shorter a particular bond, the greater its strength. Indeed studies of bond length variations have played a key role in the development of a bonding theory for molecules and crystals. Although such studies have done much to advance our knowledge of the SiO bond, our understanding of this bond is still far from complete."

Introduction

Silica, SiO_2, is used in the manufacture of glasses, molecular sieves, silicone polymers and electronic devices. High silica molecular sieves are used as selective catalysts and adsorbents and silicones are used in the manufacture of electrical insulating materials, silicone oils and greases, water repellent agents in the textile industry and lacquers used for surface protection of metals. Silica glass has properties that make it very valuable in technology. It is possibly the most perfectly elastic solid known, making it ideally suited for the manufacture of sonic delay lines in which trains of sound waves are repeatedly reflected. It is also used for suspensions in delicate instruments and for springs for weighing small objects. Silica glass is also used in the manufacture of optical wave guides and as amorphous thin films on Si. It is one of the best electrical insulators and is used in the manufacture of electrical instruments.

Because of the very compliant nature of its SiOSi angle, silica has a great tendency to form as glass. For this same reason, it also crystallizes with a variety of structure types called *polymorphs.* These include, quartz, cristobalite and tridymite and their low and high temperature forms, silicalite, keatite, the high pressure form coesite and the extremely high pressure form stishovite and a large variety of high silica molecular sieves and solid state acids. Of these silica polymorphs, coesite is an ideal material for testing theories about the nature of the SiO bond because, unlike the other the polymorphs, it contains a range of bond lengths and angles that may be compared with the predictions of a bonding model. In this exercise we will calculate the bond lengths and angles within and between the silicate tetrahedra of the silica polymorph in an attempt to learn, as predicted by quantum mechanical calculations, whether the observed SiO bond lengths correlate with the observed SiOSi angles. However, before embarking on such a set of calculations, an example calculation of bond lengths and angles will be presented for pectolite, $Ca_2NaHSi_3O_9$.

Example (1): The crystal structure of pectolite was determined by Charles T. Prewitt in 1967. Given that its cell dimensions are $a = 7.988$ Å, $b = 7.040$ Å, $c = 7.025$ Å, $\alpha = 90.51°$, $\beta = 95.18°$ and $\gamma = 102.47°$ and that the atomic coordinates (x, y, z) of Si_2 are (0.2150, 0.9544, 0.3440), that the coordinates of Si_3 are (0.4505, 0.7353, 0.1447) and that the coordinates of O_8 are (0.3955, 0.9092, 0.2746), respectively, calculate the separations between Si_2 and O_8 and Si_3 and O_8 and the $Si_2O_8Si_3$ angle.

A calculation of the two SiO bond lengths

Step 1: Calculate the metrical matrix using the observed cell dimensions of pectolite:

$$G = \begin{bmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{bmatrix} = \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix}$$

Step 2: If we denote the vectors $\mathbf{v}_1$, $\mathbf{v}_2$ and $\mathbf{v}_5$ that radiate from the origin, $\mathbf{0}$, to O_8, Si_2 and Si_3, respectively, and the vectors $\mathbf{v}_4$ and $\mathbf{v}_3$ that radiate from O_8 to Si_2 and Si_3, respectively, then the lengths of the Si_2O_8 and the Si_3O_8 bonds are equal to $|\mathbf{v}_4|$ and $|\mathbf{v}_3|$, respectively. The triple representatives of these vectors are:

$$[\mathbf{v}_1]_D = \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix}, [\mathbf{v}_2]_D = \begin{bmatrix} 0.2150 \\ 0.9544 \\ 0.3440 \end{bmatrix} \text{ and } [\mathbf{v}_5]_D = \begin{bmatrix} 0.4505 \\ 0.7353 \\ 0.1447 \end{bmatrix},$$

$$[\mathbf{v}_4]_D = [\mathbf{v}_2]_D - [\mathbf{v}_1]_D = \begin{bmatrix} 0.2150 \\ 0.9544 \\ 0.3440 \end{bmatrix} - \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix} = \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} \text{ and}$$

$$[\mathbf{v}_3]_D = [\mathbf{v}_5]_D - [\mathbf{v}_1]_D = \begin{bmatrix} 0.4505 \\ 0.7353 \\ 0.1447 \end{bmatrix} - \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix} = \begin{bmatrix} 0.0550 \\ -0.1739 \\ -0.1299 \end{bmatrix}.$$

Step 3: With the triples for $[\mathbf{v}_3]_D$ and $[\mathbf{v}_4]_D$ and the metrical matrix G, we can write the equality

$$|\mathbf{v}_3|^2 = R(Si_3O_8)^2 = [\mathbf{v}_3]_D^t G[\mathbf{v}_3]_D =$$

$$\begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} 0.0550 \\ -0.1739 \\ -0.1299 \end{bmatrix}$$

$$\begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 6.2792145 \\ -9.2294354 \\ -6.6127457 \end{bmatrix} = (1.676112)^2 \text{ and}$$

$$|\mathbf{v}_4|^2 = R(Si_2O_8)^2 = [\mathbf{v}_4]_D^t G[\mathbf{v}_4]_D =$$

$$\begin{bmatrix} -0.1805 & 0.0452 & 0.0694 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix}$$

$$\begin{bmatrix} -0.1805 & 0.0452 & 0.0694 \end{bmatrix} \begin{bmatrix} -12.4178350 \\ 4.4014173 \\ 4.3195216 \end{bmatrix} = (1.655336)^2.$$

Hence, the lengths of the Si_2O_8 and Si_3O_8 bonds are 1.655Åand 1.676Å, respectively.

A calculation of the SiOSi angle

Step 1. To find an expression for the $Si_3O_8Si_2$ angle, we form the inner product $\mathbf{v_3} \bullet \mathbf{v_4} = v_3\ v_4 \cos\angle Si_3O_8Si_2$. Solving for $\cos\angle(Si_3O_8Si_2)$, we have the expression

$$\cos\angle(\mathrm{Si_3O_8Si_2}) = ([\mathbf{v}_3]^t_D \mathrm{G}[\mathbf{v}_4]_D)/(([\mathbf{v}_3]^t_D \mathrm{G}[\mathbf{v}_3]_D)^{1/2}([\mathbf{v}_4]^t_D \mathrm{G}[\mathbf{v}_4]_D)^{1/2}) =$$

$$([\mathbf{v}_3]^t_D \mathrm{G}[\mathbf{v}_4]_D)/(R(\mathrm{Si_3O_8}) \times R(\mathrm{Si_2O_8})).$$

We next evaluate

$$([\mathbf{v}_3]^t_D \mathrm{G}[\mathbf{v}_4]_D),$$

and obtain

$$\begin{bmatrix} 0.0520 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} =$$

$$-2.009493.$$

Hence,

$$\cos\angle(\mathrm{Si_3O_8Si_2}) = -2.009493/(1.676112 \times 1.655336)$$

from which it follows that

$$\angle(\mathrm{Si_3O_8Si_2}) = 136.408°.$$

Problem (1): Write a program to calculate the bond lengths and angles for any crystal given its cell dimensions and the fractional coordinates of the atoms that comprise the bond lengths and angles. The program can be tested by calculating the SiO bond lengths and the SiOSi angle for pectolite given the observed cell dimensions and the fractional coordinates for Si and O given in the example worked above.

A calculation of the bond lengths and angles for coesite

In a study of the bond length and angle variations and the bonding in coesite, Smyth et al. (1986) collected diffraction data at 15K, determined its unit cell dimensions $a = 7.136$Å, $b = 12.384$Å, $c = 7.186$Å, $\alpha = 90.00°$, $\beta = 120.38°$ and $\gamma = 90.00°$ and the fractional coordinates of the nonequivalent Si and O atoms in the unit cell (Table 1).

Problem (2): Use your program to calculate the interatomic separations (the bond lengths, R(SiO)) between Si1 and the 4 nearest O atoms, (1.64Å$\leq$), for coesite, using the generalized coordinates given in Table 2 and show that R(Si1O1) = Å, R(Si1O3) = Å, R(Si1O4) = Å, and R(Si1O5) = Å.

Problem (3): Calculate the 6 nonequivalent OSiO angles for the $Si1O_4$ silicate tetrahedral oxyanion and show that $\angle$(O1Si1O3) = °, $\angle$(O1Si1O4) = °, $\angle$(O1Si1O5) = °, $\angle$(O3Si1O4) = °, $\angle$(O3Si1O5) = °, and $\angle$(O4Si1O5) = °.

Problem (4): Calculate the R(SiO) values for the bonds between Si2 and its 4 nearest O atoms using the coordinates given in Table 2 and show that R(Si2O2) = Å, R(Si2O3) = Å, R(Si2O4) = Å, and R(Si2O5) = Å.

Table 1: Fractional coordinates of the nonequivalent atoms in coesite

Atom	x	y	z
Si1	0.1400	0.1085	0.0721
Si2	0.5072	0.1579	0.5415
O1	0.0000	0.0000	0.0000
O2	0.5000	0.1152	0.7500
O3	0.2640	0.1245	0.9383
O4	0.3128	0.1032	0.3277
O5	0.0190	0.2118	0.4766

Table 2: Coordinates defining the SiO_4 silicate groups in coesite

Atom	x	y	z	Atom	x	y	z
Si1	x	y	z	Si2	x	y	z
O1	x	y	z	O2	x	y	z
O3	x	y	$z-1.0$	O3	$1.0-x$	y	$\frac{3}{2}-z$
O4	x	y	z	O4	x	y	z
O5	$-x$	y	$\frac{1}{2}-z$	O5	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1.0-z$

Problem (5): Calculate the nonequivalent OSiO angles for the Si2O4 group and find $\angle$(O2Si2O3) = $\quad\quad$ °, $\angle$(O2Si2O4) = $\quad\quad$ °, $\angle$(O2Si2O5) = $\quad\quad$ °, $\angle$(O3Si2O4) = $\quad\quad$ °, $\angle$(O3Si2O5) = $\quad\quad$ °, and $\angle$(O4Si2O5) = $\quad\quad$ °.

Problem (6): Using the coordinates given in Tables 3, calculate the 5 nonequivalent SiOSi angles and show the $\angle$(Si1O1Si1)= $\quad\quad$ °, $\angle$(Si2O2Si2)= $\quad\quad$ °, $\angle$(Si1O3Si2)= $\quad\quad$ °, $\angle$(Si1O4Si2)= $\quad\quad$ °, and $\angle$(Si1O5Si2)= $\quad\quad$ °.